DETERMINATION AND OCCURRENCE OF BORON IN NATURAL PHOSPHATES, SUPERPHOSPHATES, AND DEFLUORINATED PHOSPHATE ROCKS[1]

By LEWIS F. RADER, Jr., *assistant chemist*, and W. L. HILL, *associate chemist*, *Fertilizer Research Division, Bureau of Chemistry and Soils, United States Department of Agriculture*[2]

INTRODUCTION

Boron belongs to the gradually lengthening list of elements that are regarded as essential to plant growth. Recent papers review previous work on the effect of boron on plants (*1, 4, 8, 12, 26*)[3] and its occurrence in plants (*8*), soils (*8, 26*), and fertilizers including fertilizer materials (*5, 10, 11, 26*). The data for fertilizers and fertilizer materials, however, include only a few scattered results for boron in natural phosphates and superphosphates.

Results are given in this paper for boron in 54 representative samples of natural phosphates from various parts of the world, 9 samples of commercial superphosphates, and 3 samples of defluorinated phosphate rock. The results for boron in natural phosphates reported herein represent an extension of the studies of this Bureau on the composition of phosphate rock (*15, 18, 19*).

METHOD OF ANALYSIS

Chemical methods for determining boron have been classified and reviewed by Wilcox (*24*). The methods most commonly used for determining boron in minerals and fertilizers are the Chapin method (*23, p. 1691*), or some modification of it, and the official methods (*3, p. 32*). According to the Chapin method, boron is separated from the other constituents of the sample (fused with sodium carbonate, if insoluble in acid) by distillation with methyl alcohol in the presence of hydrochloric acid and of anhydrous calcium chloride as a drying agent. The methyl ester of boric acid formed in the absence of free water passes into the distillate, from which the boron is recovered in a small volume of water by saponification with alkali with subsequent removal of the alcohol by distillation. The alkaline aqueous solution of borate thus obtained is freed from carbonate and adjusted to a definite pH (6–7) after which the quantity of boron in the solution is determined by titration with standard alkali in the presence of mannitol to the pink color of the phenolphthalein indicator. In the official method for acid-soluble boron in fertilizers phosphoric acid, instead of hydrochloric acid, is used, and since phosphoric acid acts as a drying agent, this change renders the use of calcium chloride unnecessary.

The method used by the authors is substantially the method of Chapin, though the titration is in principle that of Foote (*9*). Diffi-

[1] Received for publication Sept. 14, 1938. Issued February 1939.

[2] The authors are indebted to K. D. Jacob, Fertilizer Research Division, who suggested the investigation and rendered valuable aid during the course of the work, and to J. I. Hoffman, National Bureau of Standards, for helpful suggestions on the application of the methods.

[3] Reference is made by number (italic) to Literature Cited, p. 914.

culties not met in the analysis of most materials heretofore studied are at once encountered in the application of the method to natural phosphates. Not only are the involved quantities of boron so small as to require reagents and apparatus that are sufficiently low in boron to reduce the blank correction to a very low value, but as a consequence of the presence of fluorine and silica in most natural phosphates the distillates contain relatively large quantities of hydrofluosilicic acid, which titrates in the same pH range (*17*) as does the complex of boric acid with mannitol. The authors' application of published methods to the determination of boron in fluorine-bearing phosphates and their observations on means of obviating the foregoing difficulties can be conveniently presented under the subjects: (1) Reagents, (2) titration of boric acid, (3) separation of boron from the sample, and (4) procedure used.

REAGENTS

Since the presence of fluorine in natural phosphates renders the glassware used in the course of their analysis a reagent in a very real sense, the use of borosilicate glassware is not permissible. Concentrated solutions of sodium hydroxide also become contaminated with boron from the glassware (*24*). Accordingly, Kavalier glassware (usually considered as boron-free) was used for the analytical operations and for the storage of alkaline reagent solutions. The boron content of different lots of the several reagent chemicals is shown in table 1. It may be pointed out that a 6 *M* solution of sodium hydroxide prepared from a more concentrated solution that remained in a Pyrex flask for several weeks contained far more boron (92 parts per million of B_2O_3) than did similar solutions prepared in Kavalier glass throughout (table 1).

TABLE 1.—*Boron in analytical reagents*

Reagent	B_2O_3 in reagent [1]		Reagent	B_2O_3 in reagent	
	As received	As used		As received	As used
	P. p. m.	*P. p. m.*		*P. p. m.*	*P. p. m.*
Sodium hydroxide	4	[2] 1	Calcium chloride, anhydrous for drying	53	2.4
Do	35	[2] 11	Methyl alcohol, absolute	4.5	0
Potassium hydroxide	7	[3]	Sodium carbonate	<5	<5
Do	66	[3]	Do	<5	<5
Calcium chloride, anhydrous for drying	32	.6	Mannitol	[4] 0	[4] 0

[1] Results include boron present in the hydrochloric acid used for neutralization.
[2] Milligrams of B_2O_3 per liter of 6 *M* solution.
[3] Not used.
[4] Result shown by blank titration on 2.5 g of mannitol.

A stock solution of carbonate-free sodium hydroxide (*13, p. 139*) was prepared by rinsing the sticks with distilled water to remove any surface boron arising from attack of the glass container, dissolving the rinsed sticks in an equal weight of distilled water, and allowing the solution to stand until the supernatant liquid was clear. Dilute solutions of carbonate-free sodium hydroxide were prepared as needed by diluting aliquots of this concentrated solution with recently boiled distilled water.

The reagent grades of anhydrous calcium chloride may carry appreciable quantities of boron (table 1). It was suggested [4] that the boron in this reagent probably comes from the glaze of the vessels in which it is dehydrated. Accordingly, boron from this source would appear for the most part on the surface of the granules, and its removal should be possible by extraction or volatilization. Nearly all the boron can be removed (table 1) in a single treatment by drenching 500 g of the salt in a liter copper beaker with 300 ml of 95-percent methyl alcohol containing 15 ml of concentrated hydrochloric acid and heating the well-stirred mixture on a hot plate and finally in an oven at 200° C. until the alcohol is expelled and the material again becomes anhydrous.

Absolute methyl alcohol for use in the isolation of boron from the sample was prepared by redistillation of absolute alcohol from a 3-liter Pyrex flask to which had been added a few sticks of potassium hydroxide. The presence of volatile organic acids in the alcohol would give high results for boron by the usual titration with two indicators (*13, p. 614*), and accordingly the 4.5 parts per million of B_2O_3 found in methyl alcohol as received (table 1) might be regarded merely as the B_2O_3 equivalent of the alkali consumed by such organic acids. However, the titration procedure used by the authors eliminates from the boron titration all acids that do not form complexes with mannitol, and, therefore, it would appear that boron was actually present in the alcohol. In any event the redistilled alcohol was very satisfactory.

As a matter of convenience a solution of mannitol, rather than the solid, was used in the titrations. The solution was prepared by dissolving 100 g of mannitol in recently boiled distilled water and making the volume up to 1 liter.

The sodium carbonate was used as received. Any boron in the hydrochloric acid would appear in the results for sodium hydroxide; however, the indications were that the acid contained considerably less boron than did the sodium hydroxide.

TITRATION OF BORIC ACID

In figure 1 are reproduced Foote's titration curves (*9*) for a buffered water (I) and the same containing added boric acid with (III) and without (II) mannitol. Accordingly, if the solution containing boric acid without mannitol is titrated (adjusted) until its pH value reaches some point *B* (curve II) in the pH range over which curves II and III are nearly parallel—7.6 in the present instance—a part of the boric acid will have been titrated, the alkali equivalent being $A'B'$. Then, on the addition of mannitol the pH value of the solution drops to B'' on curve III, and the titration can be completed by adding alkali (B' C' ml) until the pH value of the solution is again 7.6 at point *C*. The total alkali equivalent of boric acid is A' C', but since point A'' on curve II cannot, in general, be determined because of the limitations of indicators, as well as the presence of other acids that titrate in this pH range, the total equivalent has no meaning in actual practice.

[4] WICHERS, E. Private communication. National Bureau of Standards.

The problem, therefore, resides in the choice of the pH value to which the solution shall be adjusted before mannitol is added. For this purpose various indicators have been used; mention may be made of methyl red and paranitrophenol. With the former, the pH value lies at some point *E* on curve II; with the latter, at some point *D*. Since a different indicator, usually phenolphthalein, is used for the final titration, alkali is consumed in bringing a boron-free solution from the end point of one indicator to that of the other, which increases the blank correction to the titration. For example, Allen and Zies (*2*, *p.*

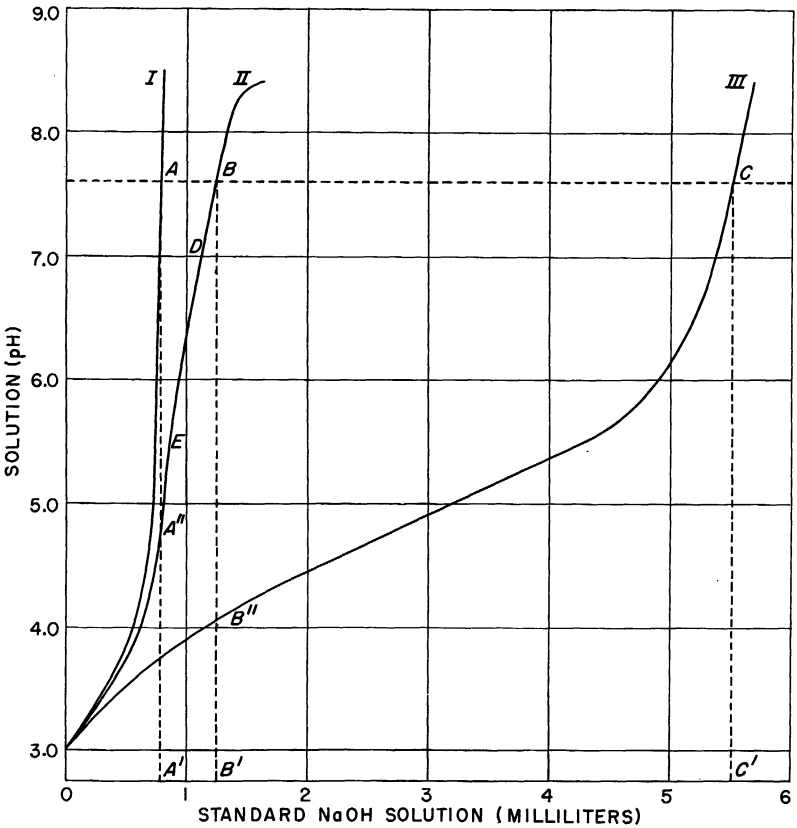

FIGURE 1.—Titration curves for boric acid (*9*). Curve I is for 50 ml of water, curve II for 50 ml of water plus 7.4 mg of B_2O_3, curve III for 50 ml of water plus 7.4 mg of B_2O_3 and 6 g of mannitol.

765) found the B_2O_3 equivalent of the alkali used in passing from the paranitrophenol end point to that of phenolphthalein to be 0.3 mg, which corresponds to a little less than 0.1 ml of 0.1 *M* sodium hydroxide, and the writers found the amount of alkali consumed between the methyl red and phenolphthalein end points to be 0.23 ml of 0.03 *M* sodium hydroxide. Furthermore, in the presence of weak acids or substances that titrate as weak acids, which are not readily separated from boric acid, as, for example, soluble fluosilicate, adjustment of the solution to a pH value in the approximate range *ED* with the necessary accuracy is extremely difficult, if not impossible. Moreover, the

titration of these same substances is continued after the addition of mannitol, thereby vitiating the result for boric acid.

The foregoing difficulties are obviated in Foote's method for the direct titration of boric acid in water (*9*) by adjusting the pH value of the solution before the addition of mannitol to the same value as that of the final end point. Since the two end points involve no pH change, other substances in solution do not interfere with the titration, except insofar as they render the end point difficult to establish. The small amount of boric acid neutralized during the initial adjustment ($A'B'$, fig. 1) is accounted for in the standardization factor of the alkali, and therefore the alkali equivalent used in practice is $B'C'$. Carbon dioxide, of course, must be excluded from the titration.

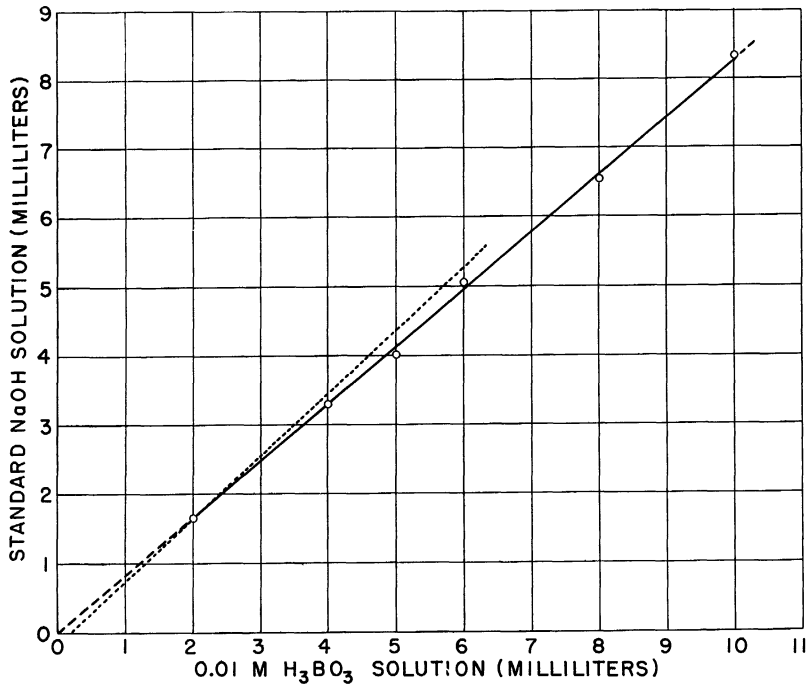

FIGURE 2.—Curve obtained in standardization of approximately 0.01 *M* sodium hydroxide against a 0.01 *M* boric acid solution with use of phenolphthalein as the indicator of both end points (10° C.). Volume of solution at initial end point was 100 ml, that at final end point was 125 ml plus the volume of standard sodium hydroxide added.

Foote adjusted his solutions to a pH of 7.6 colorimetrically with phenol red, and Wilcox (*25*) used an electrometric method. The authors used phenolphthalein, because of the comparative ease with which the end point can be recognized without accessory equipment. According to measurements with the glass electrode,[5] the faint pink of the phenolphthalein indicator in the concentration used by the authors appeared at the unusually low pH of about 7.6. In figure 2

[5] According to measurements made by L. M. White of the Fertilizer Research Division, the pH at which the faint pink color appeared in 100 ml of a 0.4 *M* solution of sodium chloride containing 20 drops of a 2-percent phenolphthalein solution was 7.6; with 10 drops of indicator the pH was 7.7, whereas with only 1 drop it was 8.4

are shown the results obtained in a typical standardization of sodium hydroxide solution against a boric acid solution prepared from fused pure boric acid (*13, p. 613*). The results fall on a straight line with a maximum deviation of about ± 0.1 ml of 0.01 *M* alkali. Since the curve passes through the origin, the blank correction is zero, as it should be with boron-free alkali, and the B_2O_3 equivalent of the alkali is obtainable directly from the slope of the curve. With an alkali containing an appreciable quantity of boron the curve would be rotated in the direction of the dotted line (fig. 2).

Besides carbon dioxide, which must always be excluded in the titration of boric acid, other known constituents of the analytical solutions obtained from natural phosphates that are likely to interfere in the subsequent titration of the boron are arsenic and fluorine. Allen and Zies (*2, p. 767*) found that the presence of 1 mg of As_2O_3 did not affect the titration of boric acid, but the presence of 25 mg rendered the phenolphthalein end point indistinct because of fading. The quantities of arsenic reported in natural phosphate (*15, p. 30*) are usually less than 0.005 percent of As_2O_3, which corresponds with 0.5 mg of As_2O_3 per 10 g of sample. Thus, if all the arsenic in the sample should follow the boron, the quantity present in the solution for titration would still be well within the tolerance indicated by Allen and Zies' results.

Quadrivalent germanium (*22*) and hexavalent tellurium (*20*) form complexes with mannitol that titrate as monobasic acids. Tellurium, like selenium, appears to be reduced to the metal in the presence of methyl alcohol, and thus it does not accompany boron in the alcohol distillate.[6] Although germanium behaves toward mannitol almost exactly as does boron, only a small fraction (probably 10 percent) of the amount of this element in the sample accompanies the boron in the final solution.[6] Thus, if the presence of germanium be neglected, the error thereby introduced in the result for boron (B_2O_3) would, because of the difference between the atomic weights of these elements, be equivalent to one-third of the germanium (GeO_2) accompanying the boron, or probably 3 to 4 percent of the germanium in the sample. Germanium has not been detected in phosphate rock, but, as far as the authors know, only two samples have been examined for this element (*14*).

The effect of fluoride and fluosilicate on the titration of boric acid apparently has not been studied to any extent heretofore. Allen and Zies (*2, p. 769*) noted some difficulty with the phenolphthalein end point in the titration of a solution obtained by distilling a synthetic mixture of boric acid and 0.2 g of NaF, whereas in a similar experiment with less fluorine (0.1 g of KF) Chapin (*23, p. 1691*) encountered no difficulty. The authors studied the effect of the presence of fluorine in quantities up to 100 mg by the addition of aliquots of a solution of sodium fluoride or hydrofluosilicic acid [7] to aliquots of standard boric acid solution and titration of the resultant solution for boron with phenolphthalein as previously indicated.

No interference was observed with sodium fluoride in the absence of notable quantities of free silica. On the other hand, with hydrofluosilicic acid pronounced fading of the indicator occurred at the

[6] HAGUE, JOHN L. Private communication. National Bureau of Standards.

[7] Prepared in the laboratory by adding an excess of pure quartz flour to c. p. hydrofluoric acid contained in a platinum dish, allowing the mixture to stand until the solution was clear, and decanting into a wax bottle.

final end point, and the result for boric acid tended to be decidedly low. This behavior is attributed to the re-formation of some fluosilicic acid as a consequence of the acidity developed in the boron-containing solution when mannitol is added to it. During the subsequent titration, the decomposition of the re-formed fluosilicic acid, which takes place slowly at the low temperature of the titration, would cause fading of the indicator and, unless the titration is continued until all the fluosilicic acid is destroyed, also a low titer for boric acid. The error arising from this source can be almost completely eliminated by continuing to add alkali until the pink of the indicator persists in the solution for at least 1 minute.

SEPARATION OF BORON FROM THE SAMPLE

The authors' recovery of added boron from synthetic mixtures and phosphate rock low in aluminum by distillation with phosphoric acid and hydrochloric acid is inclined to be 1 to 5 percent low as shown in table 2. Aluminum compounds show a marked tendency to prevent the distillation of boron, an observation also noted by others.[8] Early in the experiment, the use of phosphoric acid was discontinued because the results for acid-soluble boron obtained on phosphate rock with it were less than half the values obtained with hydrochloric acid. Later, however, it was discovered that if the rock-acid mixture is allowed to stand several hours before distillation, phosphoric acid alone gives as good results as hydrochloric acid and calcium chloride, provided only a very small quantity of water is present. For the distillation of samples that have been fused with sodium carbonate a larger quantity of phosphoric acid is needed to take care of the several milliliters of water added with the decomposed melt. The addition of phosphoric oxide (*6*) would seem preferable to the addition of larger quantities of acid.

TABLE 2.—*Recovery of boron by acid distillation*

Tabulation No.	Distillation mixture	B_2O_3			Fluorine present during titration
		Present	Found [1]	Recovered	
		Milligrams	*Milligrams*	*Percent*	*Milligrams*
1	10 ml 0.01 *M* H_3BO_3+10 ml concentrated H_3PO_4.	3.48	[2] 3.31–3.44	95.0–98.8	0
2	10 ml 0.03 *M* H_3BO_3+20 ml concentrated H_3PO_4	10.44	10.13–10.31	97.0–98.8	0
3	1 ml 0.1 *M* H_3BO_3+20 ml concentrated HCl+20 g $CaCl_2$.	3.48	3.34	96.0	0
4	10 g phosphate rock No. 912+20 ml concentrated H_3PO_4.	----------	[3] 3.34	----------	147
5	10 g phosphate rock No. 912+20 ml concentrated HCl+20 g $CaCl_2$.	----------	.33	----------	67
6	Residue in distillation flask from 5+1 ml 0.1 *M* H_3BO_3.	3.48	3.52	100	3
7	10 g phosphate rock No. 912+1 ml 0.1 *M* H_3BO_3+20 ml concentrated HCl+20 g $CaCl_2$.	[4] 3.81	3.62	95.0	97
8	Same as 7+2 g Al_2O_3	[4] 3.81	3.13	82.2	2
9	10 g No.[5] 904+1 ml 0.1 *M* H_3BO_3+20 ml concentrated HCl+20 g $CaCl_2$.	3.48	2.90	83.3	0

[1] 400 ml of distillate were collected.
[2] The first 200 ml of distillate contained 3.20 to 3.34 mg of B_2O_3, and the second 200 ml 0.06 to 0.12 mg.
[3] Rock and acid were mixed and let stand overnight before distillation.
[4] Added B_2O_3 plus B_2O_3 found in 10 g of No. 912 (tabulation No. 5).
[5] Natural aluminum phosphate.

[8] ZIES, E. G. Private communication. Geophysical Laboratory, Carnegie Institution of Washington.

Relatively large quantities of fluorine and silica usually follow the boron. The observed quantities of fluorine were indeed variable and ranged from 2 to 147 mg (table 2), depending, among other things, on the quantity of acid used, the temperature in the distilling flask, and the composition of the sample. When 20 ml of hydrochloric acid were used in the distillation the quantity of fluorine following the boron usually ranged from 40 to 90 mg.

Since fluorine in the presence of silica has an adverse effect on the titration of boric acid, some simple means of separation is highly desirable. The addition of Al_2O_3 to the distilling flask is not permissible because it holds back the boron as well as the fluorine. Double distillation with hydrochloric acid reduced the amount of fluorine in the distillate about 50 percent, and double distillation in which only 3 to 5 ml of excess hydrochloric acid and 0.05 g of $ZrOCl_2$ were added to the flask before redistilling the second time lowered it still further to 10 mg or less without affecting the results for boron. The somewhat increased precision thereby obtained was not, in the author's opinion, sufficient to justify the additional time required for analysis.

Total boron, as distinguished from acid-soluble boron obtained by direct distillation of the phosphate sample, was determined in a few typical phosphate rocks by fusing the sample with twice its weight of sodium carbonate prior to distillation (*13, p. 614*). The results by the two methods of decomposition are shown in table 3. Obviously all the boron is not, in general, completely expelled from the sample by direct treatment with acid under the conditions that prevail in the distillation. The results by the two methods on Florida land pebble and two of the three Tennessee brown rocks are in substantial agreement, whereas in other instances (except No. 904) the results for total boron are considerably higher than those for acid-soluble boron. In the case of highly aluminiferous materials, such as soft phosphate (No. 580), the difference between the results is probably attributable to the retention of boron under certain conditions by aluminum compounds, as was noted in a preceding section. Available information relating to the boron-bearing constituents of phosphates does not justify any explanation for the disparity in the results for the other phosphates (table 3). It may be merely coincidental that the latter contain either relatively large quantities of organic matter (No. 1253), or sulphide minerals (Nos. 56 and 930), or both (No. 948).

TABLE 3.—*Boron in typical phosphate rocks as determined in fused and unfused samples*

Sample No.	Source or type of phosphate	Al_2O_3	B_2O_3 determined in sample—	
			Fused with Na_2CO_3	Unfused
		Percent	*P. p. m.*	*P. p. m.*
120 [1]	Florida land pebble	0.82	24	20
912	do	1.05	28	33
908	Tennessee brown rock	1.16	40	48
1253	Idaho rock	1.16	86	45
948	Wyoming rock	1.19	107	60
930	Tennessee blue rock	1.22	81	65
56a [1]	Tennessee brown rock	1.99	54	48
56 [1]	do	3.06	77	51
580	Florida soft	23.05	60	18
904 [2]	Grand Connetable Island	36.92	<10	<10

[1] Standard sample number of the National Bureau of Standards.
[2] Natural aluminum phosphate.

PROCEDURE USED

Add 20 ml of concentrated hydrochloric acid to 10 g of the sample in a liter flask of Kavalier glass. Swirl the flask until the contents are well mixed and then allow it to stand from ½ to 1 hour with occasional swirling. At the end of this period add 20 g of purified calcium chloride to the flask and mix by swirling; then add 50 ml of redistilled absolute methyl alcohol, and after mixing the contents by rapid swirling connect the reaction flask to the distilling apparatus (*13, p. 613*). Heat the reaction flask with a free flame until the contents begin to boil, then swirl the flask a few times without disconnecting it from the condenser, and replace the flame with a water bath maintained at 80° to 90° C. for the duration of the distillation. Keep the volume of alcohol in the reaction flask as constant as possible by distilling directly into it alcohol from a second distilling flask, which should be heated to boiling temperature before inserting the reaction flask to the system. Should the reaction flask run dry, the results will be low and erratic. Regulate the rate of distillation so that 400 ml of distillate will be obtained in 45 to 60 minutes.

Receive the distillate in a 500-ml Kavalier flask containing 30 ml of distilled water and 6 ml of 6 *M* sodium hydroxide solution, and stop the distillation when the contents of the receiver reach a volume of about 450 ml. When the distillation is finished add to the distillate 0.5 ml (10 drops) of a 2-percent solution of phenolphthalein and additional 6 *M* sodium hydroxide solution as needed to develop a permanent deep pink color.

If the sodium hydroxide carries an appreciable quantity of boron it will be necessary to measure the volume of alkali used, in order to make the proper blank correction to the result for boron. Accordingly, it is convenient to add the 6 *M* alkali in 6-ml portions. Ordinarily the alkali initially added to the receiving vessel is sufficient, though in runs on aliquots of a solution of boric acid alone and not infrequently with rock samples an additional 6 ml is required, and occasionally, when an unusually large quantity of fluorine distills over, as much as 18 ml of alkali will be needed.

After the addition of an excess of alkali to the distillate, distill off the alcohol by immersing the flask in a water bath with due care to avoid superheating at the beginning of distillation. Boiling tubes are indispensable here. When alcohol no longer distills over, transfer the pink residual aqueous solution directly to a 300-ml Kavalier flask for titration. It is not necessary to evaporate the solution to dryness and ignite the residue, as is done in the analysis of plant materials (*24*). Adjust the volume of the solution to 100 ml with water and boil the alkaline solution from 4 to 5 minutes on a hot plate to expel any residual alcohol before it is made acid incident to the removal of carbonate.

Render the hot alcohol-free solution acid with hydrochloric acid by adding concentrated acid until nearly all the excess alkali is neutralized, then 0.1 *M* acid to neutrality, and finally about 1 ml of 0.1 *M* acid in excess. Boil the acidified solution about 3 minutes with several vigorous swirlings during this period; make the solution faintly alkaline with 1 *M* alkali, then acid with 0.1 *M* hydrochloric acid, using 6 drops in excess, and reboil as before. Again restore the pink

color of the indicator with alkali, discharge it with 0.1 *M* acid, using this time only 2 drops in excess, boil again, and then cool the nearly neutral carbonate-free solution to 10° C. by placing the stoppered flask in a bath of ice water.

It is considered good practice to guard against a possible loss of boron during the boiling of the acidified solution by connecting the flask to an air condenser. The stepwise approach to the neutral point with intervening boiling not only increases the precision of the method but also lowers the blank titration on the reagents.

Adjust the cold (10° C.) milky solution accurately to the initial end point by adding 0.03 *M* sodium hydroxide solution to a permanent faint pink color, keeping the flask stoppered as far as possible to prevent the ingress of carbon dioxide, then add 25 ml of a 10 percent solution of mannitol. Boil the solution from 3 to 4 minutes with occasional swirling, again cool it to 10° C., and titrate it at this temperature with 0.03 *M* sodium hydroxide solution until the faint pink of the indicator persists for at least 1 minute. The result for boric oxide is obtained by multiplying the volume of sodium hydroxide solution (corrected for the blank titration on the reagents) consumed in the titration after the addition of mannitol by the factor for the alkali found by standardization against pure boric acid, the same titration procedure being used.

When only 6 ml of 6 *M* alkali was added to the alcohol distillate, the blank titration on the reagents amounted to 0.1 ml of 0.03 *M* sodium hydroxide, or 13 p. p. m. of B_2O_3 on the basis of 10 g of sample, which agrees well with the value (11 p. p. m.) expected from the analyses of the purified reagents (table 1). Furthermore, in the presence of the usual quantities of fluorine and silica the precision of the titration is also about 0.1 ml of 0.03 *M* sodium hydroxide. Accordingly, when the corrected titer was only 0.1 ml, the result is arbitrarily reported as $\leqq$10 p. p. m., whereas with a smaller titer the result is reported as $<$10 p. p. m.

Duplicate determinations of boron in the fluorine-bearing phosphates usually agreed within 15 p. p. m., the average difference being 8 p. p. m. Agreement was closer in the case of fluorine-free materials.

BORON IN NATURAL PHOSPHATES

Results for acid-soluble boron in domestic and foreign phosphates are given in tables 4 and 5, respectively. For the few results for total boron, as determined by fusing the sample with sodium carbonate, reference must be made to table 3. The data in tables 4 and 5 are summarized according to type of phosphate in table 6. South Carolina rock ranks first in quantity of boron and the African rocks second, each of these types of phosphate averaging more than 90 p. p. m. of B_2O_3. At the other extreme is bone ash, Florida soft and waste-pond phosphates, and Russian apatite, with less than 20 p. p. m. With the exception of the phosphatic limestone the averages for all other types of phosphate examined range from 42 to 61 p. p. m. of B_2O_3, inclusive.

TABLE 4.—*Acid-soluble boron in domestic phosphates*

Sample No.	Type of phosphate	Location of deposit	P_2O_5	B_2O_3
			Percent	*P. p. m.*
FLORIDA PHOSPHATES				
618	Land pebble	Pierce	30.53	98
619	do	Nichols	30.98	67
910	do	Mulberry	31.09	75
947	do	Brewster	31.28	72
790	do	Not known	31.40	70
912	do	Mulberry	35.37	33
120 [1]	do	do	35.40	20
1447 [2]	do	Bartow	35.11	54
1310 [3]	do	Not known	34.43	63
771	Hard rock	do	31.25	60
932	do	Dunnellon	35.99	40
580	Soft	Not known	29.49	18
728	do	Juliette	31.80	<10
581	Waste pond	Not known	18.18	<10
915	do	Dunnellon	23.63	<10
SOUTH CAROLINA PHOSPHATES				
495	Not known	Not known	16.07	63
1139	Land rock	Bulow mines, Johns Island	26.92	126
1138	do	Lamb's mine, near Charleston	27.85	142
1137	do	do	27.58	144
TENNESSEE PHOSPHATES				
56 [1]	Brown rock	Not known	31.28	51
56a [1]	do	Mount Pleasant	32.94	48
762	do	do	33.72	53
906	do	Wales	34.39	36
908	do	Mount Pleasant	34.44	48
1401 [3]	do	Wales	36.73	70
772	Blue rock	Glover	30.45	66
930	do	Gordonsburg	30.97	65
1049	Kidney	Boma	31.22	56
1048	White rock	Tomscreek	30.20	55
1031	do	Godwin	35.80	57
917	Phosphatic limestone	Gordonsburg	11.68	30
WESTERN PHOSPHATES				
550	Light colored	Idaho, Paris	32.21	67
1011	do	Montana, Garrison	27.63	32
1009	do	do	31.39	22
1252	do	do	36.38	48
1010	do	do	37.47	40
948	Dark colored	Wyoming, Cokeville	30.19	60
973	do	Idaho, Conda	32.53	70
1253	do	do	32.13	45
OTHER PHOSPHATES				
1295	Apatite	Virginia, Amherst County	39.58	47
971	Bone ash		40.36	17

[1] Standard sample number of the National Bureau of Standards.
[2] Concentrated by oiling and tabling.
[3] Concentrated by froth flotation.

TABLE 5.—*Acid-soluble boron in foreign phosphates*

Sample No.	Location of deposit	P_2O_5	B_2O_3
		Percent	*P. p. m.*
AFRICAN PHOSPHATES			
1559	Algeria, Djebel Kouif	30.00	116
1549	Egypt, Safaga	32.79	110
553	Morocco	34.30	66
1551	Tunis, Gafsa	29.05	84
INSULAR PHOSPHATES			
452	Christmas Island	39.46	46
985	Curaçao Island	38.59	70
904 [1]	Grand Connetable Island	54.51	<10
1230	Makatea Island	37.94	72
450	Nauru Island	38.92	55
451	Ocean Island	40.32	37
APATITES			
905	Canada, Quebec Province	40.30	≦10
1305	Union of Soviet Socialist Republics, Kola Peninsula	31.63	12
1304	do	37.39	20

[1] Natural aluminum phosphate.

TABLE 6.—*Acid-soluble boron in different types of natural phosphates*

Type or source of phosphate	Samples analyzed	B_2O_3	
		Range	Average
	Number	*P. p. m.*	*P. p. m.*
DOMESTIC PHOSPHATES			
Florida land pebble	9	20–98	61
Florida hard rock	2	40–60	50
Florida soft and waste pond	4	<10–18	<12
South Carolina	4	63–144	119
Tennessee brown rock	6	36–70	51
Tennessee blue and white rocks and kidney phosphate	5	55–66	60
Tennessee phosphatic limestone	1	----------	30
Western part of the United States:			
Light-colored rock	5	22–67	42
Dark-colored rock	3	45–70	58
Apatite from Virginia	1	----------	47
Bone ash	1	----------	17
FOREIGN PHOSPHATES			
Africa	4	66–116	94
Islands	[1] 5	37–72	56
Apatite from the Union of Soviet Socialist Republics	2	12–20	16

[1] Excluding the sample (No. 904) of natural aluminum phosphate.

The authors' results for boron in phosphate rock are considerably lower than most of the figures reported in the literature. Young (*26, p. 32*), using the official method (*3, p. 32*) for acid-soluble boron, found 450 p. p. m. of B_2O_3 in a sample of Florida hard rock, only traces in two other Florida phosphates of unknown type, and 450 and 580 p. p. m. in two Tennessee brown rocks. The spectrochemical results of Gaddum and Rogers (*10*) are much higher. Thus, the latter authors report the equivalent of 0.16 to 1.6 percent of B_2O_3 in Florida pebble and soft phosphates. On the other hand, recent spectrochemical anlyses, made with extreme care by B. F. Scribner of the National Bureau of Standards (*14*), showed only 0.005 percent of B_2O_3 and <0.001 percent of B_2O_3, respectively, in a Tennessee brown rock (National Bureau of Standards standard sample No. 56a) and a

Florida land pebble (National Bureau of Standards standard sample No. 120). The results agree well with the authors' figures for these samples as shown in table 4.

At present, little can be said concerning the boron-bearing minerals occurring in natural phosphates. Schaller (*21, p. 168*) has prepared a list of all the known boron minerals including 56 names comprised in 2 groups, viz, 36 borates and 20 borosilicates. Many of these minerals are soluble in water and a large majority of them are either soluble in, or are decomposed by, hydrochloric acid. Several of the borosilicates, as, for example, tourmaline, are not decomposed by hydrochloric acid, though in the analysis of phosphate rock their decomposition would be promoted by the fluorine present in the sample. So far as the authors are aware, only one boron mineral has been identified in phosphate rock. A very small quantity of tourmaline was found (*15, p. 76*) in one sample of Florida land pebble (No. 912).

BORON IN SUPERPHOSPHATES AND DEFLUORINATED PHOSPHATE ROCK

In view of the presence of considerable quantities of fluorine in most natural phosphates and the volatility of boron fluoride, it would be difficult to predict the fate of the boron in phosphate rock during the manufacture and storage of superphosphate. In general, one might expect the boron to distribute itself between the superphosphate and the gases expelled when the rock and acid are mixed and during subsequent storage of the superphosphate. On the other hand, if boron-free acid were used and no boron were volatilized during manufacture, the boron content of the resulting superphosphate would, in the case of ordinary superphosphate, be roughly 50 percent of that of the ingredient rock. Thus, on the basis of the data in table 6, ordinary superphosphates prepared from Florida land pebble and Tennessee brown rock, respectively, would probably contain 10 to 50 and 18 to 35 p. p. m. of B_2O_3. These figures agree reasonably well with the amounts found by analysis (table 7).

TABLE 7.—*Acid-soluble boron in superphosphates and defluorinated phosphate rocks*

SUPERPHOSPHATES

Sample No.	Phosphatic fertilizer		P_2O_5	B_2O_3
	Type	Made from—		
			Percent	*P. p. m.*
1403[1]	Ordinary superphosphate	Florida land pebble	20.56	<10
1402[2]	do	do	20.60	<10
1580	do	do	20.85	51
1581	do	Tennessee brown rock	20.24	36
1486	Special superphosphate[3]	Florida land pebble	32.67	58
1361	Double superphosphate	do	49.27	94
1481	do	Tennessee brown rock	43.43	77
1362	do	do	48.87	158
1372	do	Idaho rock	47.33	96

DEFLUORINATED PHOSPHATE ROCKS

1476[4]	Fused phosphate rock	Tennessee brown rock	28.95	21
1351	Calcined phosphate rock	do	36.58	20
1478	do	do	37.25	30

[1] The sulphuric acid used in the preparation of this superphosphate was processed sludge acid from the raffination of asphalt-base petroleum.

[2] The sulphuric acid used in the preparation of this superphosphate was untreated sludge acid from the raffination of asphalt-base petroleum.

[3] Prepared by granulating a mixture of ordinary and double superphosphate.

[4] Defluorinated in the fused condition (*7*).

The agreement of the results in the foregoing comparison relating to ordinary superphosphate leaves the inference that in the manufacture of phosphoric acid by the wet process a large part of the boron in the phosphate rock may go into the product acid. Accordingly, double superphosphate made with such phosphoric acid would be expected to contain as much, or more, boron than the ingredient rock. The results for boron in double superphosphates (table 7), in comparison with the boron content of the same types of phosphate rock (table 6), clearly support this expectation.

Results for boron in domestic superphosphates reported by previous workers (*10, 26*) are considerably higher than the figures obtained by the authors, the differences being about the same as were found in the case of phosphate rock.

Without asserting that previously reported results are subject to such error, it should be pointed out in this connection that superphosphate, because of the presence of active fluorine compounds, readily attacks glass and cannot be stored in glass bottles without becoming contaminated with boron from the container. For the sake of comparison, results on portions of double superphosphates No. 1361 and 1362 that had stood in glass bottles for 3 years may be cited. Samples taken from the center of these bottles, that is, out of direct contact with the glass, showed 120 and 186 p. p. m. of B_2O_3, respectively, as compared with 94 and 158 p. p. m. (table 7) in material that was stored in wooden containers.

The quantity of acid-soluble boron found in defluorinated Tennessee brown-rock phosphate (*7, 16*) amounted to 20 to 30 p. p. m. of B_2O_3 (table 7), and since this material is almost completely decomposed by hydrochloric acid, these figures may be regarded as a close approach to the total boron. On the basis of the range of the results for brown rock (table 6) it appears that around 50 percent of the boron in phosphate rock is volatilized in the defluorination process. Defluorinated phosphate rock probably carries less boron than basic slag. An imported slag (not shown in the tables), the only slag examined by the authors, contained 116 p. p. m. of B_2O_3.

SUMMARY

The Chapin method, modified to the extent that only one indicator is required in the titration, was applied to the determination of the relatively small quantities of boron occurring in natural phosphates and superphosphates.

Results are given for boron in 54 samples of natural phosphates from various deposits of the world, 9 samples of superphosphates, and 3 samples of defluorinated phosphate rock. The results for acid-soluble boron (B_2O_3) in natural phosphates range from <10 to 144 p. p. m., in superphosphates from <10 to 158 p. p. m. and in defluorinated phosphate rock from 20 to 30 p. p. m.

LITERATURE CITED

(1) ANONYMOUS.
1935–36. BORON AND PLANT LIFE. Fert., Feed. Stuffs, Farm Supplies Jour. 20: 720–722, 724, 748–752, illus., 1935; 21: 4–6, 8, 60–62, 64, illus., 1936.

(2) ALLEN, E. T., and ZIES, E. G.
1918. A CONTRIBUTION TO THE METHODS OF GLASS ANALYSIS, WITH SPECIAL REFERENCE TO BORIC ACID AND THE TWO OXIDES OF ARSENIC. Jour. Amer. Ceram. Soc. 1: [739]–786, illus.
(3) ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.
1935. OFFICIAL AND TENTATIVE METHODS OF ANALYSIS. . . . Ed. 4, 710 pp., illus. Washington, D. C.
(4) BERTRAM, P.
1935. DIE BEDEUTUNG EINIGER SPURELEMENTE FUER DIE PFLANZEN. 4th Cong. Internatl. Tech. et Chim. des Indus. Agr. Bruxelles, v. 2, pp. 396–414, illus.
(5) BRECKPOT, RAYMOND.
1935. DOSAGE SPECTROGRAPHIQUE DE CERTAINS CONSTITUANTS SECONDAIRES DU NITRATE DE SOUDE DU CHILI. 4th Cong. Internatl. Tech. et Chim. des Indus. Agr. Bruxelles, v. 2, pp. 382–388, illus.
(6) CALFEE, R. K., and MCHARGUE, J. S.
1937. OPTICAL SPECTROGRAPHIC DETERMINATION OF BORON: POLARIZING ATTACHMENTS. Indus. and Engin. Chem., Analyt. Ed. 9: 288–290, illus.
(7) CURTIS, HARRY A., COPSON, RAYMOND L., BROWN, EARL H., and POLE, GORDON R.
1937. FERTILIZER FROM ROCK PHOSPHATE: CONVERSION BY FUSION AND TREATMENT WITH WATER VAPOR. Indus. and Engin. Chem. 29: 766–770, illus.
(8) EATON, FRANK M.
1935. BORON IN SOILS AND IRRIGATION WATERS AND ITS EFFECT ON PLANTS WITH PARTICULAR REFERENCE TO THE SAN JOAQUIN VALLEY OF CALIFORNIA. U. S. Dept. Agr. Tech. Bull. 448, 132 pp., illus.
(9) FOOTE, FRED J.
1932. DETERMINATION OF BORON IN WATERS: METHOD FOR DIRECT TITRATION OF BORIC ACID. Indus. and Engin. Chem., Analyt. Ed. 4: 39–42, illus.
(10) GADDUM, L. W., and ROGERS, L. H.
1936. A STUDY OF SOME TRACE ELEMENTS IN FERTILIZER MATERIALS. Fla. Agr. Expt. Sta. Bull. 290, 15 pp.
(11) HANCE, F. E.
1933. REPORT ON CHEMISTRY. Hawaii. Sugar Planters Assoc. Proc. 53 (Rept. Com. in Charge Expt. Sta.): 46–63.
(12) HILL, H.
1936. MINOR ELEMENTS AFFECTING HORTICULTURAL CROPS. Sci. Agr. 17: 148–153, illus.
(13) HILLEBRAND, W. F., and LUNDELL, G. E. F.
1929. APPLIED INORGANIC ANALYSIS; WITH SPECIAL REFERENCE TO THE ANALYSIS OF METALS, MINERALS, AND ROCKS. 929 pp., illus. New York and London.
(14) HOFFMAN, JAMES I., and LUNDELL, G. E. F.
1938. THE ANALYSIS OF PHOSPHATE ROCK. Natl. Bur. Standards Jour. Research 20 (5): 607–626, illus.
(15) JACOB, K. D., HILL, W. L., MARSHALL, H. L., and REYNOLDS, D. S.
1933. THE COMPOSITION AND DISTRIBUTION OF PHOSPHATE ROCK WITH SPECIAL REFERENCE TO THE UNITED STATES. U. S. Dept. Agr. Tech. Bull. 364, 90 pp.
(16) ——— REYNOLDS, D. S., and MARSHALL, H. L.
1936. PHOSPHATE FERTILIZERS BY CALCINATION PROCESS—VOLATILIZATION OF FLUORINE FROM PHOSPHATE ROCK AT HIGH TEMPERATURES. Amer. Inst. Mining and Metall. Engin. Tech. Pub. 695, 14 pp., illus.
(17) KERN, EDWARD F., and JONES, THOMAS R.
1930. TITRATION OF FLUOSILICIC AND FLUOBORIC ACIDS. Amer. Electrochem. Soc. Trans. 57: 273–278, illus.
(18) MARSHALL, H. L.
1934. THE OCCURRENCE OF FERROUS IRON IN PHOSPHATE ROCK. Jour. Agr. Research 49: 71–76.

(19) RADER, LEWIS F., Jr., and HILL, W. L.
1935. OCCURRENCE OF SELENIUM IN NATURAL PHOSPHATES, SUPERPHOSPHATES AND PHOSPHORIC ACID. Jour. Agr. Research 51: 1071–1083.
(20) ROSENHEIM, ARTHUR, and WEINHEBER, M.
1911. ZUR GRAVIMETRISCHEN BESTIMMUNG DES TELLURS UND ALKALIMETRISCHEN BESTIMMUNG DER TELLURSÄURE. Ztschr. Anorgan. Chem. 69: 266–269.
(21) SCHALLER, WALDEMAR T.
1930. BORATE MINERALS FROM THE KRAMER DISTRICT, MOHAVE DESERT, CALIFORNIA. U. S. Geol. Survey Prof. Paper (1929) 158: 137–170, illus.
(22) TCHAKIRIAN, ARAKEL.
1928. DOSAGE TITRIMÉTRIQUE DE L'ACIDE GERMANIQUE, ÉTUDES DE QUELQUES FORMES HYDRATÉES DE CET ACIDE ET DE SES SELS. Compt. Rend. Acad. Sci. [Paris] 187: 229–231.
(23) WHERRY, EDGAR T., and CHAPIN, W. H.
1908. DETERMINATION OF BORIC ACID IN INSOLUBLE SILICATES. Jour. Amer. Chem. Soc. 30: 1687–1701, illus.
(24) WILCOX, L. V.
1930. DETERMINATION OF BORON IN NATURAL WATERS AND PLANT MATERIALS. Indus. and Engin. Chem., Analyt. Ed. 2: 358–361, illus.
(25) ———
1932. ELECTROMETRIC TITRATION OF BORIC ACID. Indus. and Engin. Chem., Analyt. Ed. 4: 38–39.
(26) YOUNG, R. S.
1935. CERTAIN RARER ELEMENTS IN SOILS AND FERTILIZERS, AND THEIR RÔLE IN PLANT GROWTH. N. Y. (Cornell) Agr. Expt. Sta. Mem. 174, 70 pp.